Master's Thesis

Nitrate-based aprotic electrolyte for reversible Li-CO_2 battery

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(Battery Science and Technology)

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Contents

Abstract

Recently, the Li-CO_2 batteries have emerged as fascinating energy storage system because of capturing CO_2 and converting into valuable energy. However, the Li_2CO_3 as the discharge product has insulating property in Li-CO_2 batteries where exhibits more sluggish decomposition reaction kinetics, and it leads to the increase of the overpotential during charging. In this study, we demonstrate reversible operation of the Li-CO_2 battery with $LiNO_3$-based aprotic electrolyte. Our quantitative study on in-situ differential electrochemical mass spectrometry (DEMS) investigation with $LiNO_3$-based electrolyte in Li-CO_2 battery reveals the equal consumption/evolution of CO_2 gases during discharge/charge process. Li-CO_2 battery using $LiNO_3$-based electrolyte shows the two-electron reversible reaction. In particular, the NO_3^- ions acts redox mediator during discharge/charge process where efficiently changes the reaction route from irreversible 1.33 e^-/CO_2 to reversible 2.00 e^-/CO_2. And we demonstrate the discharge product, which is the Li_2CO_3, according to X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy (Raman) results. This study indicates that the $LiNO_3$-based electrolyte offer highly reversible Li-CO_2 operation with redox-shuttle effect.

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Chapter 1

1.1 Introduction of Li-CO_2 battery

Over time, the negative effect of carbon dioxide (CO_2) gases, the most dominant greenhouse gas, on the atmospheric warming has been increasing because of the excessive use of fossil fuels.[1] To convert CO_2 gas into other organic compounds, a significant energy input is needed because carbon atom has the highest oxidation state.[2] In order to fix CO_2, various products are obtained, including methanol,[3] ethylene[4] and carbon monoxide.[5] Nevertheless, these chemicals require further compression process treatment to store and transport conveniently. This process gives rise to additional energy consumption. Accordingly, fixing CO_2 could suggest an alternative by using renewable energy in an energy storage device.

Intriguingly, a study on Li-CO_2 battery has been emerged in recent years.[6] Because Li-CO_2 batteries can capture CO_2 gas, which has been used to store the energy as an energy carrier. Generally, Li-CO_2 batteries compose of a Li metal anode, an electrolyte, a separator and a carbon-based cathode. The electrochemical reaction in Li-CO_2 batteries are expressed as $4Li + 3CO_2 \leftrightarrow 2Li_2CO_3 + C$ (E^o= 2.8 V, Figure 1.1), where Li_2CO_3 and C (carbon) are the main discharge products in a pure CO_2 environment.[6-9]

Figure 1.1 The schematic illustration of Li-O_2 and CO_2 battery's structure/mechanism

However, the decomposition of Li_2CO_3 requires high energy owing to its insulating properties and results in an increased overpotential. The high overpotential causes the further decomposition of the electrolyte, leading to the reducing of the amount of electrolyte in the battery and then the side reaction and poor cycling stability of the battery. These significant problems negate the advantages of Li-CO_2 batteries.[10]

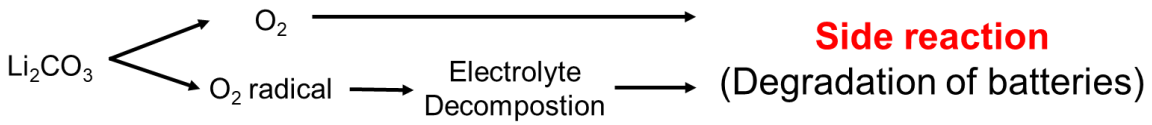

Figure 1.2 The schematic illustration of side-reaction during decomposition of Li_2CO_3

To improve Li-CO_2 battery performance, the discharge product must be efficiently decomposed, and the decomposition reactions of the electrolyte must be suppressed. Recently, many studies have been focusing on the improvement of electrode design, catalyst, and electrolyte to address the challenges on Li-CO_2 batteries.

1.2 Trends of Li-CO_2 battery studies

1.2.1 Electrodes

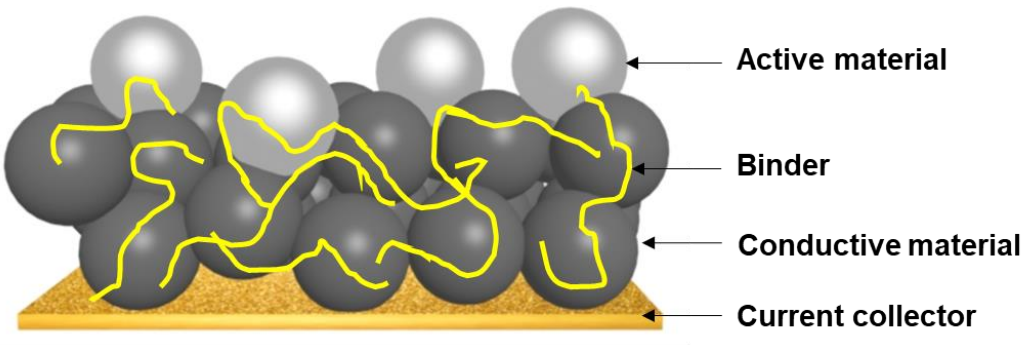

Figure 1.3 The schematic illustration of electrode components.

Electrodes consist of an active material, a binder, a conductive material, and a current collector. (Figure 1.2) The conductive material, usually using carbon materials, transports the electrons which are generated after the electrochemical reaction, from the active materials to the current collector. The electric flow interference, resulting from the decomposition of the electrolyte and the electrode, causes the overpotential and the cell performance degradation.[11] Therefore, studies have been conducted on using high conductivity electrodes that prevent the decomposition of the electrode.

Dai's groups have recently proposed the anodes in which graphene, a high specific surface area and conductivity material, is doped with heteroatoms (B, N).[12]

Subsequently, the carbon nanotubes (CNT), owing to its high porosity and conductivity, has been reported to obtain higher cycle performance of the battery than graphene. These cathodes have long-term cycle stability than only carbon-based cathodes.[13-14]

However, the problem of those approaches is that traces of Li_2CO_3 still remains after long-term cycling. In addition, the cycle and capacity do not reach the level of Li-CO_2 battery use. Therefore, Li-CO_2 battery has been studied various cathodes and catalysts to reduce overpotential and to improve cycle performance through reversible reactions.

1.2.2 Kinds of catalysts

Carbon-based cathodes require a lot of energy for Li_2CO_3 insulator decomposition. Also, there is the concern that the unnecessary energy released would cause overpotential resulting in the decomposition of the electrode and the electrolyte. To achieve reversible Li_2CO_3 decomposition, studies are being conducted on using carbon-based cathode with catalysts.

Catalysts are synthesized by novel metals or transition metals and used to enhance the decomposition of the Li_2CO_3 discharge product. Studies have been performed using catalysts in Li-CO_2 batteries. Catalysts on electrodes have been used to improve battery performance and efficiency through higher capacity and lower overpotential than carbon-based cathodes.[15-21]

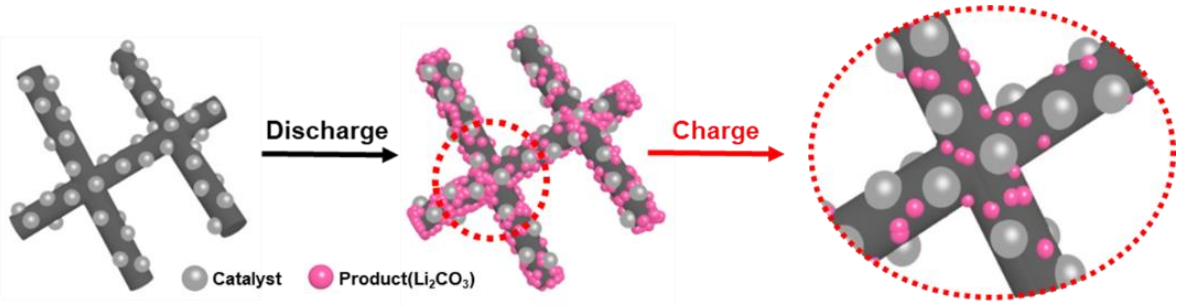

Figure 1.4 The schematic illustration of catalyst's challenge.[21]

Nevertheless, there is a problem in which small amounts of Li_2CO_3 still remain after long-term cycling. In this phenomenon, the areas of adjacent to the catalyst can easily decompose Li_2CO_3 discharge product, but the areas that are far from the catalyst cannot decompose easily (Figure 1.4). Studies are being conducted to increase the catalytic reactivity of catalysts that are highly dispersible, and more progress is needed. Furthermore, most catalysts are expensive owing to their scarcity, and only the adjacent areas of existing dispersed catalyst electrodes are decomposed. [19-21]

To compensate for these shortcomings, this study elucidates a redox mediator, which is dissolved in a solvent, lowers overpotential, and increases reactivity with the product.

1.2.3 Redox mediators (RMs)

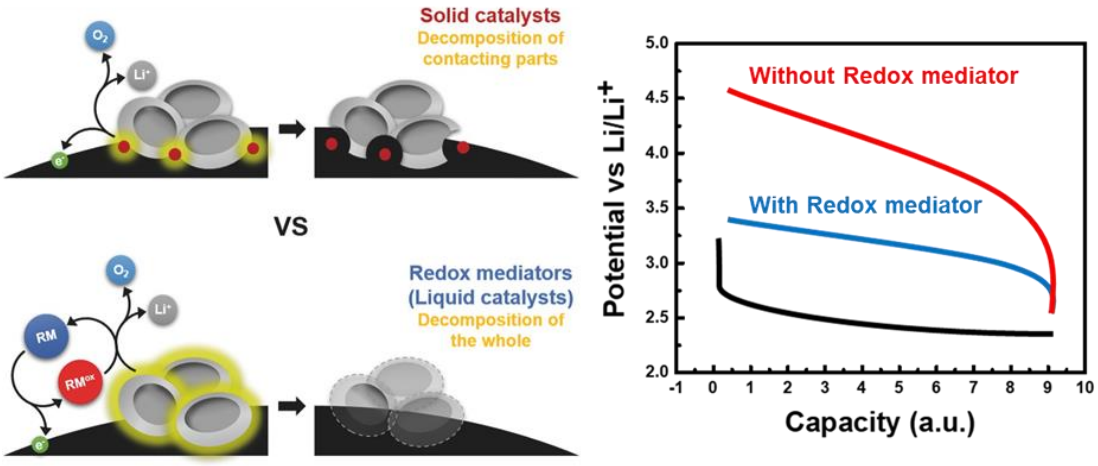

Figure 1.5 The schematic of principle & function of redox mediator.[22]

RM stands for "redox mediator", and directly participates in the redox reaction. RM not only reduces the de-composition-activation energy of the discharge products but also acts as a catalyst during the charge process. As a catalyst dissolves in an organic solvent, it increases contact areas with the discharge product and selectively decomposes only the product. In addition, an RM has the advantage of allowing the battery to operate via a reversible reaction through directly engaging in the electrochemical reaction (Figure 1.5).[22]

Of the various types of RMs, studies have been reported on the active use of halogen and/or aromatic materials, which are stabilized after accepting or contributing electrons. The use of those RMs assist the stable redox reaction occurring within a low voltage range during the cycling of the batteries.[23]

To overcome these problems of Li-CO_2 battery studies, LiBr[24] and binuclear cobaltphtalocyanine[25] have been used. It reduced the overpotential than conventional organic solvent electrolytes, and Li_2CO_3 was completely decomposed.

However, RMs react with lithium metal electrodes, and side reactions occur, due to their vulnerability of Li metal and reductive RMs.[26] These challenges must be improved in order for Li-CO_2 batteries to run.

Currently, studies on Li-CO_2 batteries are actively being conducted. Because there is scarce study data on Li-CO_2 battery, most of the Li-CO_2 battery studies have been conducted by referring to previous Li-O_2 battery studies.

In order to improve the decomposition of Li_2CO_3 as the main discharge product and operate reversible reactions without side-reactions; there is on-going research on electrodes, catalysts, RMs and various electrolytes to overcome the problem of Li-CO_2 batteries.

1.3 Goal for in this research

This study used the $LiNO_3$-based aprotic electrolyte, in which $LiNO_3$ salt used in Li-O_2 battery, to increase the stability of the electrodes and improve the cycle performance of the battery.

Among the various studies to improvement performance that have been operated to reduce overpotential and pre-vent side-reactions in Li-O_2 batteries, there have used $LiNO_3$ salt with dimethylacetamide (DMAc) solvent.

Li_2O forms on the electrode through the interaction between lithium metal anode and NO_3^- anion, and is a chemically stable solid electrolyte interphase (SEI) layer. The SEI layer prevents additional reactions from occurring on the electrode surface and produces ideal oxygen evolution reaction.[27-29] In the case of $LiNO_3$-based electrolytes, previous studies have operated batteries without the side-reactions caused by the $LiNO_3$ salt's redox effect.[30-31] DMAc solvents have a high donor number, and they can stabilize radical species.[32]

This study shows the advantages of $LiNO_3$ and DMAc solvent in Li-CO_2 batteries in order to resolve the irreversible reactions problem associated with Li-CO_2 batteries. XPS, SEM (scanning electron microscope), and Raman were used to analyze the discharge products and to measure CO_2 consumption with the DEMS analysis[33] method.

1.4 Result and discussion

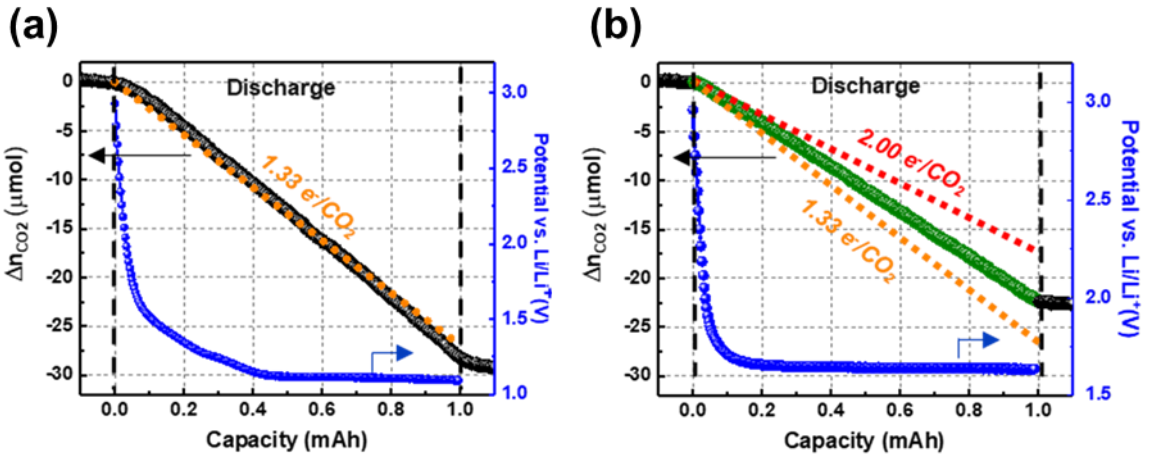

Figure 1.6 The quantities of CO_2 gas consumption occur during discharge. a) uses the LiTFSI in TEGDME electrolyte. b) uses the $LiNO_3$ in the DMAc electrolyte. The blue line in both graphs indicates the potential. Black and green lines indicate CO_2 gas consumption during discharge. (The orange dotted line is the gas consumption according to 1.33 electron process. The red dotted line is the gas consumption according to 2.00 electron process.)

Figure. 1.6 a) is a graph that depicts the LiTFSI-based Li-CO_2 battery operating at a constant current of 200 μA. The graph shows the voltage and the amount of CO_2 consumed during discharge using the DEMS method. Figure 1.6 b) shows the measurements of the amount of CO_2 gas that is consumed when a $LiNO_3$-type Li-CO_2 battery is discharged at a constant current of 200 μA.

Previous Li-CO_2 battery studies have shown a ($4Li + 3CO_2 \leftrightarrow 2Li_2CO_3 + C$) mechanism of 1.33 e^-/CO_2, but the $LiNO_3$ type electrolyte shows around 1.7 e^-/CO_2. This electron process shows a different trend than previous studies. Therefore, several analysis techniques were used to confirm that the Li-CO_2 battery's main product Li_2CO_3 was produced without additional reactions during discharge.

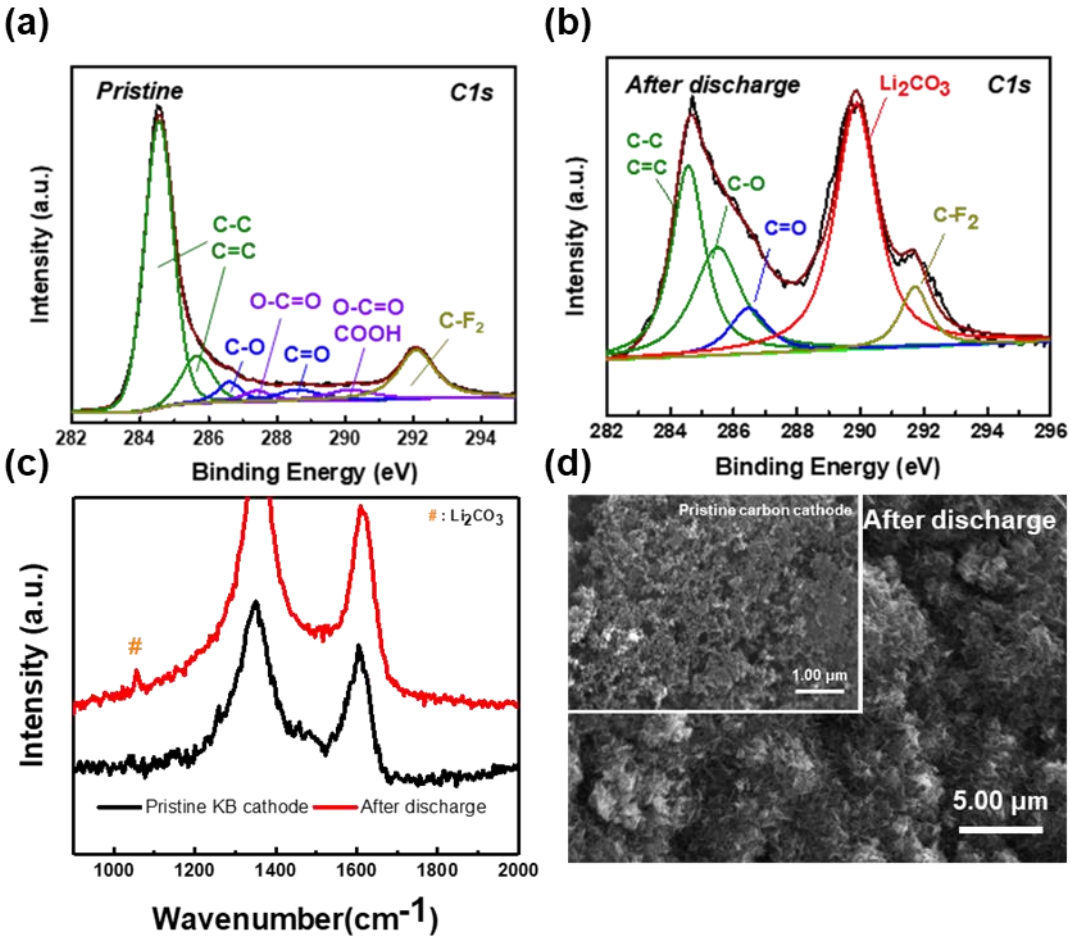

Figure 1.7 Discharge product analysis in $LiNO_3$-based electrolyte using a) and b) XPS, c) Raman and SEM, applying a current of 200 μA for 5 hours. a), b) are the XPS data of pristine cathode and after discharge respectively. c) is the Raman data. (the black line is the pristine cathode, the red line is the after discharge, while the orange symbol (#) is the Raman peak of Li_2CO_3 ~1088 cm^{-1})

Figure 1.7 is XPS, Raman, and SEM analysis to show the discharge product of the $LiNO_3$ type Li-CO_2 battery. Figure 1.7 a) shows the XPS analysis technique to measure the electrode before discharge, and Figure 1.7 b) shows the XPS results for the electrode surface specimen after discharge. When compared with Fig. 1.7 a), a peak (~290 eV) for Li_2CO_3 can be seen in Fig. 1.7 b). Fig. 1.7 C) shows a Li_2CO_3 peak (~1080 cm^{-1}) after discharge using the Raman analysis method.[6,17,21,34-35] Additional products were not seen in either the XPS or the Raman results. This can be interpreted to mean that the $LiNO_3$-type Li-CO_2 battery mainly produces Li_2CO_3. Fig.1.7 d shows the SEM analysis technique. After discharge, the product appears as a film on the carbon electrode. Based on the XPS and Raman analysis, Li_2CO_3 appears to be the discharge product of the $LiNO_3$-type Li-CO_2 battery.

This study shows that the $LiNO_3$-type battery produces Li_2CO_3 as the main product at 1.7 e^-/CO_2, unlike in previous studies.

DEMS analysis was used to measure potential and the amount of CO_2 that was produced during the $LiNO_3$-type battery charging.

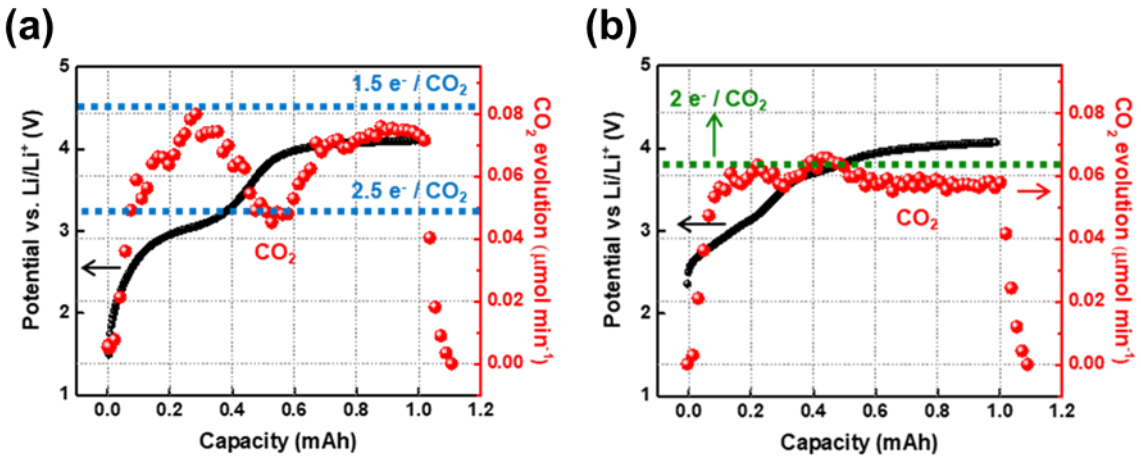

Figure 1.8 The first charge and CO_2 gas evolution profiles of Li-CO_2 cell, applying a current of 200 μA for 5 hours obtained using DEMS analysis in a) the LiTFSI-based electrolyte and b) the $LiNO_3$-based electrolyte after 1.0 mAh discharged at pure CO_2 atmosphere.

Fig. 1.8 a) shows the changes in the CO_2 amount and change in potential that occurred when the $LiNO_3$-type battery was charged at a current of 200 μA. When the Li-CO_2 battery used the conventional electrolyte, most of the potential rapidly increased to more than 4.0 V.[6,36] The generated CO_2 tended to vary according to the potential. In these experiments, the $LiNO_3$-type battery charged at around 4.0 V, and the generated CO_2 approached 2.00 e^-/CO_2 (0.062 μmol/min).(figure 1.8b) Based on these results, the $LiNO_3$-type Li-CO_2 battery shows lower overpotential and more fixed CO_2 generation than the Li-CO_2 battery.

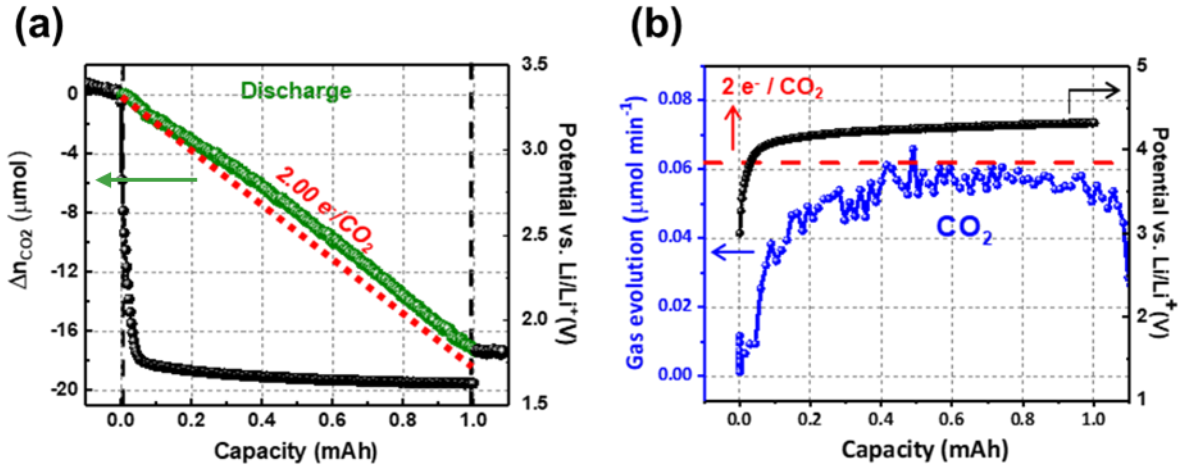

Figure 1.9 The first discharge a) and charge b) profiles with high concentration 3 M $LiNO_3$ in DMAc electrolyte. CO_2 gas reduction and oxidation profiles during discharge and charge process of Li-CO_2 cell, applying a current of 200 μA for 5 hours obtained using in-situ DEMS analysis.

Up to now, the mechanism by which CO_2 is fixed and generated before and after charging and discharging has been analyzed. The nitrate-type electrolyte appears to have an intermediate value between a 1.33 and a 2.00-electron process during discharge. During charging, a 2.00-electron process occurs in fig 1.6b and fig 1.8b. We assume that Eq. 1 and the nitrate effect occur simultaneously in the mechanism of CO_2 consumption during discharge.

Therefore, in order to increase the nitrate effect, experiments were performed with a concentration of salt that was higher than that of previous experiments. Fig 1.10 a) shows the CO_2 consumption and potential during discharge. The graph shows that the actual consumed amount was ~ 2.10 e^-/CO_2, which is close to a 2.00-electron process. Fig 1.9 b) shows the gas and potential that occurred during charging. The CO_2 occurred at 0.062 μmol min^{-1} (2.00 e^-/CO_2) as it did previously. No additional gasses other than CO_2 occurred.

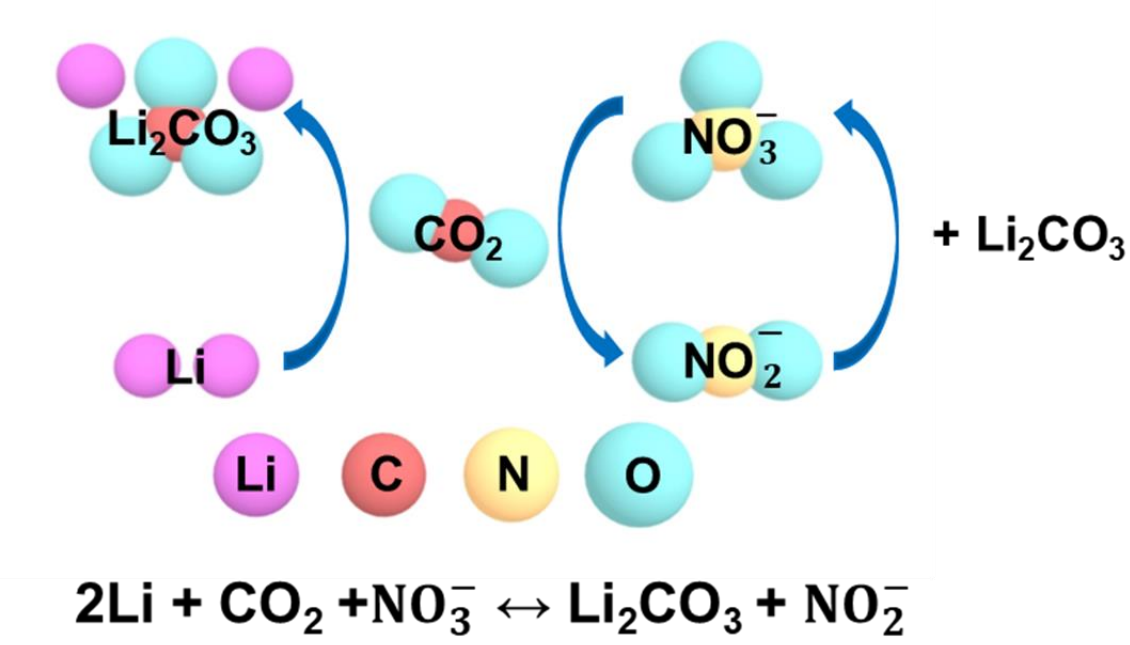

Figure 1.10 Schematic illustration of the suggestion mechanism in Li-CO_2 using $LiNO_3$-based electrolyte.

Among Li-CO_2 batteries, there have been no reports of $LiNO_3$-based batteries, and the mechanism that was found is not certain. This experiment aims to measure CO_2 consumption/generation and describe the consumption/generation mechanism. The $LiNO_3$-based Li-CO_2 battery has an ~ 1.70 e^-/CO_2 electron process, which is between 1.33 e^-/CO_2 and 2.00 e^-/CO_2 during discharge. During charging, CO_2 generation is fixed at 2.00 e^-/CO_2 without generating any additional gasses. High-concentration $LiNO_3$-based batteries show a reversible electron process at 2.00 e^-/CO_2 during charging and discharging.

In the Li-air studies reported, $LiNO_3$-based batteries have a 2.00 electron process through the interaction of NO_3 anions. Based on this mechanism, the $LiNO_3$-based Li-CO_2 battery mechanism is shown in Fig. 1.10. In the proposed mechanism, two lithium atoms react with CO_2 to create the main product Li_2CO_3. The NO_3 anion changes to an NO_2 anion, and the O contributes to the main reaction. Moreover, the NO_2 anion performs the role of a catalyst that decomposes the Li_2CO_3 during charging and becomes an NO_3 anion again. According to the proposed mechanism, the $LiNO_3$-based Li-CO_2 battery has a reversible reaction, and it creates a charging reaction at a lower overpotential through the redox-shuttle effect of the nitrate anion.

1.6 Conclusion

It is difficult to obtain a reversible reaction involving CO_2 in Li-CO_2 batteries during electrochemical reactions. In this study, a reversible reaction was obtained using a nitrate-based electrolyte. CO_2 consumption and evolution exhibited a two-electron process during both the charge and the discharge.

It was also confirmed that the process is maintained at high-concentration conditions. Moreover, XPS and Raman analysis confirmed that only Li_2CO_3 was produced without additional products.

Thus far, there have been no reports of nitrate-based electrolytes in research regarding Li-CO_2 batteries to the best of our knowledge. There is also insufficient research on the interactions of electrolytes with CO_2. This study presents the possibility of applying a new mechanism and a new electrolyte in Li-CO_2 batteries, based on which various electrolytes can be developed with reference to Li-O_2 battery, as it is necessary to develop Li-CO_2 batteries exhibiting reversible reactions and low overpotential.

1.7 Experimental section

Li–CO_2 Cell Assembly. For the preparation of the cathode for the aprotic electrolyte, the air cathode was fabricated using a mixture of Ketjenblack carbon (EC-300J) and polytetrafluoroethylene (PTFE, Sigma-Aldrich, USA) at 9:1 (wt%). The mixture was dispersed in water solution and cast on an SUS mesh (stainless steel mesh, Shinmyung Science Inc.) current collector, and then was dried at 120 ℃ in a vacuum oven overnight. The cathode loading mass was approximately 0.3 mg/cm^2.

1 M LiTFSI (Lithium bis(trifluoromethanesulfonyl)imide) in the TEGDME (Tetraethylene glycol dimethyl ether) and 1 M $LiNO_3$ in the DMAc (dimethylacetamide) were purchased from Enchem (Korea) and stored in an Ar-filled glove box (H_2O and O_2 < 1 ppm).

3 M $LiNO_3$ in the DMAc were fabricated using $LiNO_3$ salt (Sigma Aldrich, ReagentPlus) and DMAc solvent (Sigma Aldrich, anhydrous 99.8%). The Li-CO_2 cell was assembled into a 2032 coin cell (Hohsen, CR2032, Japan) with holes. The Li metal film (thickness of 0.3 mm) was purchased from FMC (Korea). The glass fiber separator (GF/C) was purchased from Whatman (England). The Li-CO_2 cell assembly was carried out in an Ar-filled glove box.

Material Characterizations The carbon cathode were analyzed by using a SEM (S-4800, Hitachi High Technologies, Japan) at an acceleration voltage of 5.0 kV and XPS experiments were performed on a scanning X-ray microprobe (ESCALAB 250XI, Thermo Fisher scientific, US). Raman spectra were measured by a micro Raman spectroscope (alpha 300, WITec GmbH) using 532 nm. Before the cathodes were transferred to SEM and XPS analysis after cell disassembly, they were packed in an Ar-filled glove box to prevent contamination of products on electrode from the air.

Electrochemical Measurements. Galvanostatic discharge-charge was used to evaluate battery performance (capacity, voltage, power density) by using a battery cycler system (WBCS 3000, WonATech, Korea). For the experiments performed, the Li-CO_2 cells using aprotic electrolytes were tested at room temperature in a lab-built coin cell kit. The details of the differential electrochemical mass spectrometer (DEMS) system are described elsewhere.[33]

References

1. Matter, J. M.; Stute. M.; Snæbjörnsdottir. S. O.; Oelkers. E. H.; Gislason, S. R.; Aradottir, E. S.; Sigfusson, B.; Gunnarsson, I.; Sigurdardottir, H.; Gunnlaugsson, E.; Axelsson, G.; Alfredsson, H. A.; Wolff-Boenisch, D.; Mesfin, K.; Taya, D. F. d. l. R.; Hall, J.; Dideriksen, K.; Broecker, W. S., Rapid carbon mineralization for permanent disposal of anthropogenic carbon dioxide emissions. *Science* **2016**, 352, 1312-1314

2. Rochelle, G. T., Amine scrubbing for CO2 capture. *Science* **2009**, 325, 1652-1654

3. Graciani, J.; Mudiyanselage, K.; Xu, F.; Baber, A. E.; Evans, J.; Senanayake, S. D.; Stacchiolar, D. J.; Liu, P.; Hrbek, J.; Sanz, J. F.; Rodriguez, J. A., Catalysis. Highly active copper-ceria and copper-ceria-titania catalysts for methanol synthesis from CO2. *Science* **2014**, 345, 546-550

4. Ren, D.; Deng, Y.; Handoko, A. D.; Chen, C. S.; Malkhandi, S.; Yeo, B. S., Selective electrochemical reduction of carbon dioxide to ethylene and ethanol on copper(I) oxide catalysts. *ACS Catal* **2015**, 5, 2814-2821

5. Costentin, C.; Drouet, S.; Robert, M.; Savéant, J.-M., A local proton source enhances CO2 electroreduction to CO by a molecular Fe catalyst. *Science* **2012**, 338, 90-94

6. Qiao, Y.; Yi, J.; Wu, S.; Liu, Y.; Yang, S.; He, P.; Zhou, H., Li-CO2 Electrochemistry: A New Strategy for CO2 Fixation and Energy Storage. *Joule* **2017**, voulme 1, Issue 2, 11, 359-370

7. Xu, S.; Das, S. K.; Archer, L. A.,The Li–CO2 battery: a novel method for CO2 capture and utilization. *RSC advances* **2013**, 3 (18), 6656-6660

8. Takechi, K.; Shiga, T.; Asaoka, T., A Li–O2/CO2 battery. *Chemical communications* **2011**,47 (12), 3463-3465

9. Li, J.; Zhao, H.; Qi, H.; Sun, X.; Song, X.; Guo, Z.; Tamirat, A. G.; Liu, J.; Wang, L.; Feng, S., Drawing a Pencil-Trace Cathode for a High-Performance Polymer-Based Li–CO2 Battery with Redox Mediator. *Adv. Funct. Mater.***2019**, 29, 1806863

10. Yang, S.; He, P.; Zhou, H., Exploring the electrochemical reaction mechanism of carbonate oxidation in Li–air/CO2 battery through tracing missing oxygen. *Energy Environ. Sci* **2016**, 9, 1650

11. Wang, Y.; Cho. S. C., Analysis of Air Cathode Perfomance for Lithium-Air Batteries. *Journal of The Electrochemical Society* **2013**, 160 (10) A1847-A1855

12. Qie, L.; Connell, J. W.; Xu, J.; Dai, L., Highly rechargeable Li-CO2 batteries with a boron and nitrogen-codoped holey graphene cathode. *Angew.Chem.Int.Ed* **2017**, 56, 6970–6974

13. Zhang, X.; Zhang, Q.; Zhang, Z.; Chen, Y.; Xie, Z.; Wei, J.; Zhou, Z., Rechargeable Li-CO2 batteries with carbon nanotubes as air cathode. *Chem. Commun* **2015**, 51, 14636-14639

14. Li, Y.; Zhou, J.; Zhang, T.; Wang, T.; Li, X.; Jia, Y.; Cheng, J.; Guan, Q.; Liu, E.; Peng, H.; Wang, B., Highly surface wrinkled and N-doped CNTs anchored on metal wire. *Adv. Funct. Mater* **2019**, 29, 1808117

15. Zhang, Z.; Zhang, Z.; Liu, P.; Wie, Y.; Cao, K.; Zhou, Z., Identification of cathode stability in Li–CO2 batteries with Cu nanoparticles highly dispersed on N-doped graphene. *J. Mater. Chem. A* **2018**, 6, 3218-3223

16. Pipes, R.; Bhargav, A.; Manthiram, A., Nanostructured Anatase Titania as a Cathode Catalyst for Li–CO2 Batteries. *ACS Appl. Mater. Interfaces* **2018**, 10, 43, 37119-37124

17. Zhang, X.; Wang, C.; Li, H.; Wang, W. -G.; Chen, Y. -N.; Xie, Z.; Zhou, Z., High performance Li–CO2 batteries with NiO–CNT cathodes. *J. Mater. Chem. A* **2018**, 6, 2792-2796

18. Hou, Y.; Wang, J.; Liu, L.; Liu, Y.; Chou, S.; Shi, D.; Liu, H.; Wu, T.; Zhang, W.; Chen, J., Mo2C/CNT: An Efficient Catalyst for Rechargeable Li–CO2 Batteries. *Adv. Funct. Mater* **2017**, 27, 1700564

19. Yang, S.; Qiao, Y.; Liu, Y.; Cheng, Z.; Zhu, J. -J.; Zhou, H., A reversible lithium–CO2 battery with Ru nanoparticles as a cathode catalyst. *Energy Environ. Sci* **2017**, 10, 972-978

20. Bie, S.; Du, M.; He, W.; Zhang, H.; Yu, Z.; Liu, J.; Liu, M.; Yan, W.; Zhou, L.; Zhou, Z., Carbon Nanotube@RuO2 as a High Performance Catalyst for Li–CO2 Batteries. *ACS Appl. Mater. Interfaces* **2019**, 11, 5, 5146-5151

21. Liang, H.; Zhang, Y.; Chen, F.; Jing, S.; Yin, S.; Tsiakaras, P., A novel NiFe@NC-functionalized N-doped carbon microtubule network derived from biomass as a highly efficient 3D free-standing cathode for Li-CO2 batteries. *Applied Catalysis B: Environmental* **2019**, 244, 559-567

22. Park, J. -B.; Lee, S. H.; Jung, H. -G.; Aurbach, D.; Sun, Y. -K., Redox Mediators for Li–O2 Batteries: Status and Perspectives. *Adv.Mater* **2018**, 30, 1704162

23. Kwak, W. -J.; Kim, H.; Jung, H. -G.; Aurbach, D.; Sun, Y. -K., Review—A Comparative Evaluation of Redox Mediators for Li-O2 Batteries: A Critical Review. *Journal of The Electrochemical Society* **2018**, 165 (10) A2274-A2293

24. Wang, X. -G.; Wang, C.; Xie, Z.; Zhang, X.; Chen, Y.; Wu, D.; Zhou, Z., Improving Electrochemical Performances of Rechargeable Li-CO2 Batteries with an Electrolyte Redox Mediator. *ChemElectroChem* **2017**,4, 2145–2149

25. Li, J.; Zhao, H.; Qi, H.; Sun, X.; Song, X.; Guo, Z.; Tamirat, A. G.; Liu, J.; Wang, L.; Feng, S., Drawing a Pencil- Trace Cathode for a High- Performance Polymer- Based Li–CO2 Battery with Redox Mediato. *Adv. Funct. Mater* **2019**, 29, 1806863

26. Lee, S. H.; Park, J. -B.; Lim, H. -S.; Sun, Y. -K., An Advanced Separator for Li–O2 Batteries: Maximizing the Effect of Redox Mediators. *Adv. Energy Mater* **2017**, 7, 1602417

27. Uddin, J.; Bryantsev, V. S.; Giordani, V.; Walker, W.; Chase, G. V.; Addison, D., Lithium Nitrate As Regenerable SEI Stabilizing Agent for Rechargeable Li/O2 Batteries. *J. Phys. Chem. Lett* **2013**, 4, 21, 3760-3765

28. Xia, C.; Kwok, C. Y.; Nazar, L. F., A high-energy-density lithium-oxygen battery based on a reversible four-electron conversion to lithium oxide. *Science* **2018**, 361, 777–781

29. Yoo, E.; Qiao, Y.; Zhou, H., Understanding the effect of the concentration of LiNO3 salt in Li–O2 batteries. *J. Mater. Chem. A* **2019**, 7, 18318–18323

30. Giordani, V.; Tozier, D.; Uddin, J.; Tan, H.; Gallant, B. M.; McCloskey, B. D.; Greer, J. R.; Chase, G. V.; Addison, D., Rechargeable-battery chemistry based on lithium oxide growth through nitrate anion redox. *Nature Chemistry* **2019**, volume 11, 1133–1138

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32. Walker, W.; Giordani, V.; Uddin, J.; Bryantsev, V. S.; Chase, G. V; Addison, D., A Rechargeable Li–O2 Battery Using a Lithium Nitrate/N,N-Dimethylacetamide Electrolyte. *J. Am. Chem. Soc* **2013**, 135, 6, 2076-2079

33. McCloskey, B. D.; Bethune, D. S.; Girishkumar, G.; Luntz, A. C., Solvents' Critical Role in Nonaqueous Lithium–Oxygen Battery Electrochemistry. *J. Phys. Chem. Lett* **2011**, 2, 10, 1161-1166

34. Wood, K. N.; Teeter, G., XPS on Li-Battery-Related Compounds: Analysis of Inorganic SEI Phases and a Methodology for Charge Correction. *ACS Appl. Energy Mater* 2**018**, 1, 9, 4493-4504

35. Pasierb, P.; Komornicki, S.; Rokita, M.; Rekas, M., Structural properties of Li2CO3–BaCO3 system derived from IR and Raman spectroscopy. *Journal of Molecular Structure* **2011**, Volume 596, Issues 1–3, 26, 151-156

36. Zhang, Z.; Wang, X. G.; Zhang, X.; Xie, Z.; Chen, Y. N.; Ma, L.; Peng, Z.; Zhou, Z., Verifying the Rechargeability of Li-CO2 Batteries on Working Cathodes of Ni Nanoparticles Highly Dispersed on N-Doped Graphene. *Adv. Sci* **2018**, 5, 1700567